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Chemistry and Physics of Glass

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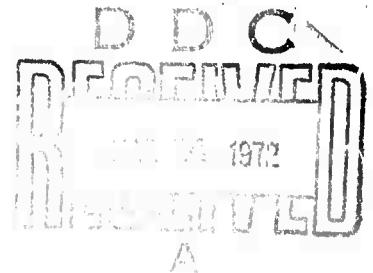
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I. Introduction

This report summarizes work completed under the sponsorship of ARPA Order No. 418 during the last half of 1971. The program is divided into two areas of research, (1) the structure of glass and (2) the mechanical properties of glass.

There have been several significant developments in the past six months. A comprehensive study of the structure of SiO_2 by x-ray diffraction techniques indicates that silica glass is composed nearly entirely of ordered regions similar to the crystalline polymorph tridymite. This is sharply in contrast with the random network theory which has long been applied to glasses. Work on other glass systems also indicates ordering out to as far as 20Å. These glasses are apparently composed of small crystallites bonded together in random orientations.

Recent measurements on ion implanted silica indicate that the strength increases by as much as 50% in samples with surface concentrations of $10^{21}/\text{cm}^3$ implanted species. This is the first evidence of strength increase by high energy ion stuffing. The NRL high purity laser glass has been successfully prepared in larger melts and will be tested for damage threshold. A computer program for analysis of vibrations in a two dimensional A_2B_3 disordered network has been generated in order to study crack propagation in layered structures. In addition, an investigation of infrared transmitting glasses is now underway.

II. Progress

Structure of Glass

The nature of the atomic arrangements in glassy solids has been given a variety of descriptions. In one model a portion of the material

is pictured as composed of small regions of crystalline-like order bonded together in essentially random orientations. In another model the material is depicted as a random network where only a few of the shortest interatomic distances correspond throughout the sample to those present in a crystalline phase. Both models picture the glass as a continuous network and differ only in the degree of local atomic ordering.

The limited atomic ordering recognized in previous diffraction analysis of silica glass, a presumably characteristic glassy material, has been generally interpreted as supporting a random network model. However, subtle difficulties in the analysis can seriously interfere with the interpretation of the results of a diffraction experiment for the longer distances. These difficulties arise in part from the limitations of the experimental data with respect to both the restricted range of scattering angle and accuracy. In addition, certain interferences can arise from the treatment of the data and the subsequent Fourier analysis. Special analytical procedures have been developed at NRL to largely overcome these limitations so that a relatively small, but potentially important, quantity of information concerning the longer interatomic distances can be obtained with confidence.

Both x-ray and neutron data have been collected with a high degree of accuracy. Employing the newly developed techniques for the treatment of these data has revealed greater atomic ordering than has previously been reported. The radial distribution functions contain significant detail out to at least 13Å in contrast with earlier studies that indicated no details beyond 7Å.

Analysis of these radial distribution functions has indicated that the experimental silica glass data are consistent with a structure composed nearly entirely ^{of} ordered regions similar to the crystalline polymorph tridymite having dimensions of about 13A and bonded efficiently together in configuration analogous to twinned crystals.

An additional indication that small-scale crystalline-like ordering exists in glasses is given by preliminary results at NRL for the glass of As_2Se_3 which shows that this glass possesses considerable short range order with detail in the radial distribution function out to about 20A. This ordering appears essentially the same as that of the known crystal structure.

Glass Preparation

The study of the contamination of glass by platinum was terminated in the present reporting period. The last report disclosed the composition of a new laser glass host with specifications for its preparation and analytical evidence for its freedom from platinum. It pointed out, however, that the procedure of melting in a reducing atmosphere could leave reducible impurities such as zinc, lead and some others in a metallic state and that such reduced metals might behave as damage sites in laser glass. Some evidence of such behavior has now been observed. A glass sample was subjected to laser radiation until damage consisting of a series of internal bubbles was produced. The sample was next ground down to expose the inner surface of a large bubble and then examined with an electron beam microprobe. Zinc was found in the damaged area. Regrinding the sample to expose another bubble produced the same result. The

role of zinc as a damage producing impurity seems reasonable in light of its reducibility in the carbon monoxide melting atmosphere, but while zinc may be a relatively likely impurity in glass making raw materials its presence had never been reported in the routine analysis of our glasses.

In light of the above observation it appeared of interest to determine whether a melting arrangement could be devised which would maintain metal impurities such as zinc as dissolved oxide constituents of the glass and still prevent platinum contamination. The single experiment performed with this contention appeared very promising. A portion of the alkali content of a glass preparation was provided as the oxidizing agent sodium nitrate, and melting was done in an argon atmosphere. Microscopic examination of the glass surface failed to reveal the presence of platinum. Neither the retention of nitrate by the glass nor the damage threshold of the glass has been investigated, but the absence of platinum contamination in the presence of an oxidizing agent is a very encouraging result. Other oxidizing agents are probably more suitable for this procedure. Cerium, an ingredient of laser glass, would be an obvious choice. While this work is very interesting and promises to be of importance, it is not being pursued in light of a change in the sponsor's interests.

Work on the strengthening of glass by copper cladding or by valence variation has not succeeded in demonstrating an improvement in glass strength. While adherent copper mirrors were produced in early experiments the process employed did not prove to be reproducible, and a uniform set of samples for strength testing has not been obtained. The use of valence variation has not yet proved to be of benefit. Glass strengthening by this process is dependent upon

the production of compressive stress in a glass surface due to its expansion upon the reduction of some of the glass ions to a lower valence state with attendant expansion.

Its success requires that oxygen not be lost by the glass in the reduction process and that the reduction be made at temperatures below the strain point in order that the compressive stresses not be annealed out. Alternatively if loss of oxygen is found to accompany the reduction, strengthening might be achieved by an oxidation process with accompanying gain in oxygen.

A set of six samples of a vanadium containing glass were obtained in which the reduction of surface vanadium by hydrogen treatment was demonstrated by luminescence changes. However no improvement in strength was observed when these samples were compared to a control group of the same glass composition which had not received the surface reduction treatment. Failure to achieve strengthening could be due to loss of oxygen in the reduction process which would result in a surface contraction rather than the desired expansion, or it could be due to annealing during the reduction process. A new set of samples is now being processed at a lower reduction temperature at which annealing is less likely. If failure to achieve strengthening is due to oxygen loss, an oxidation procedure rather than reduction is indicated, but no suitable glass composition is available for the oxidation process at the present time. In one experiment it was shown that it might be possible to develop a glass containing divalent chromium in order to demonstrate the oxidation process, but in light of the impending termination of support for this work, this phase of the effort is not being pursued.

The investigation of infrared transmitting glasses is now underway. The work began with the measurement of the infrared transmission in

the 10.6μ region of available samples of chalcogenide glasses. The best samples had no easily detected absorption in this region, but all had an absorption at about 13μ which has been ascribed to oxygen impurity. Since this 13μ band could conceivably be responsible for a weak absorption at 10.6μ an investigation of the oxygen contamination of such glasses was planned, but has not been pursued in light of lack of sponsor encouragement. Instead an investigation of infrared transmitting glasses for shorter wavelengths is being made. First glasses being studied are aluminates. These glasses are reported in a patent and by Barr and Stroud Ltd. of Scotland as transmitting in the visible and in the infrared to $5-6\mu$. Water produces an absorption near 3μ which is eliminated by vacuum melting. The glass has been manufactured in this country by a process which does not eliminate the water absorption. All glasses previously reported have absorption in the visible and near ultraviolet regions. We have already established that the above absorption is due to platinum impurity, and employing our technique of melting in a reducing atmosphere, have produced water clear glass samples which transmit in the ultraviolet to at least 250 nm. Our samples have some infrared absorption due to water which will probably require a vacuum melting process to remove. These glasses have poorer chemical durability than silicate glasses, but their softening temperatures and strengths resemble those of silicate glasses rather than chalcogenides.

A problem in the preparation of those glasses is their tendency to devitrify unless they are rapidly quenched. Rapid quenching is not easily accomplished in reducing atmosphere melting. The main present activity is to develop a composition which will be compatible with reducing atmosphere melting and will resist devitrification. Following this development the removal of water absorption, and the effect of impurities upon infrared absorption will be studied.

Other infrared glasses to be investigated in the program will be heavy metal containing glasses, antimonates, and tellurides. These materials have been reported as infrared transmitting in small quenched samples, but have much lower softening points than the aluminates. Preliminary efforts will be to attempt the development of devitrification resistant compositions of higher softening points.

Ion Implantation Effects on the Strength of Silica Glass

During this period we have increased irradiation times to achieve surface concentrations on the 10^{20} - $10^{21}/\text{cm}^3$ range. This work has been done using a small Van de Graaff at 60 KeV accelerating potential. The combination of large sample size combined with high dose makes it difficult to get access to the big machine because of long run times and high cost per sample. Silica samples show evidence of surface radiation damage at these high doses. Optical absorption bands at 5.3 and 5.8 eV are similar to the E' centers observed in x-irradiated SiO_2 . This assignment is confirmed by the presence of an ESR signal at $g = 2.0007$ due to E' centers.

In the last report the problem of radiation compaction of fused silica under irradiation was discussed. Scientists at the NRL Van de Graaff have observed such effects in thin ion implanted silica samples. These specimens tend to warp with radiation dose due to the stress produced by surface contraction. This is a tensile stress which is directly opposed to the end result we are seeking by the ion implantation. The densification process saturates at a density of $2.26\text{gm}/\text{cm}^3$ vs an initial density of $2.21\text{gm}/\text{cm}^3$ roughly a 2% increase in density. This makes SiO_2 a poor candidate for our experiments. In spite of this drawback, recent experiments with SiO_2 disks implanted with

$10^{20} - 10^{21}$ ions/cm³ have indicated biaxial tensile strength increases of up to 50%. It should be noted that it has not been possible to separate the radiation effects on the glass strength from those of the surface compression, but this will be attempted in the next few months. Plans are underway to try a recently developed NPL technique utilizing laser light scattered off acoustical surface waves propagating along the glass surface to measure the stress gradient in the sample. This is not presently possible since the 2 micron penetration depth of the ions is too small for resolution at the ultrasonic frequencies now available.

Disks of borosilicate glasses (Corning 7740) have recently been prepared instead of silica for the ion implantation experiments. The statistical distribution of tensile failure stress vs sample number is not as narrow as in the SiO₂ ($\pm 20\%$ vs $\pm 7\%$) but is sufficiently well defined to allow for the observation of significant increases in strength after ion bombardment. These samples should not tend to densify like fused silica. It also seems worthwhile to measure the strength of chemically strengthened glass before and after ion implantation. If the stress effects are additive, this might allow us to achieve very high strength glasses. These experiments are planned on Corning aluminosilicate glass, which has been ion exchanged using molten potassium salts.

Theory of Disordered Systems

The work described in the previous report concerning the vibrations of the glass-like two-dimensional disorder A₂B₂ network is nearing completion. Computer programs have been written which successfully generate the coordinates of every atom in the network,

set up the dynamical matrix for a particular choice of force constants, and calculate the vibrational spectrum and eigenvectors for particular frequencies. The calculations have been applied to the layer-type vitreous chalcogenides As_2S_3 and As_2Se_3 in order to obtain the force constants and to assign the observed absorptions to specific vibrational modes. Spectra for a trial system of 265 atoms have been calculated using mass, force constant and bond distance appropriate to these materials. The calculated spectrum is remarkably close to the far infrared spectrum of the glasses in both intensity and peak positions. Work to date indicates that the Raman spectrum of As_2Se_3 and As_2S_3 can also be fit quite well by the model. The limited size of the CDC-3800 core storage ($\approx 35,000$ words) is at present the biggest problem. This restriction severely limits the depth of information that can be obtained. The object of this study was to do at least a crude calculation concerning the change of free energy associated with crack propagation in a prototype glass. We had also hoped to be able to relate the temperature dependence of the Gaussian infrared absorption lineshapes of As_2Se_3 to changes in the Gaussian distribution of As-Se-As bond angles. These studies are statistical in nature and require a large model system. Present memory capacity allows us to fit the peak positions and intensity of the infrared and Raman spectra of As_2Se_3 and As_2S_3 and thereby obtain force constants. We can also still calculate eigenvectors and assign the observed absorptions to specific normal modes. The remainder of this work depends on access to larger core storage if and when that becomes available.

The work on the surface chemistry of SiO_2 is being extended to study the Raman spectrum of BCl_3 chemisorbed on silica gel. This

is part of a continuing effort to prepare water resistant chemical layers on glass. This NRL work has been summarized in a recent paper on chemisorption in the BCl_3 - SiO_2 system. It has been proposed that isolated hydroxyls form a non-bridging species $\equiv\text{Si}-\text{O}-\text{BCl}_2$, geminal groups a bridging species $=\text{Si}(-\text{O}-)_2\text{BCl}$ and hydrogen-bonded hydroxyls another bridging species $(\equiv\text{Si}-\text{O}-)_2\text{BCl}$. The Raman spectra of chemisorbed BCl_3 should provide a further test for the proposed model.

III. Contract with Bausch and Lomb

A extension of the contract with Bausch and Lomb until April 1, 1972 at no cost is being negotiated. Work under this contract is still concerned with the preparation of 400 gram samples of the NRL developed laser glass. Two preliminary samples have been delivered and await testing. Bausch and Lomb have made two changes in the NRL preparation procedure. These include a minor modification of the glass composition and the use of a 1500°C melting temperature which is 100°C higher than the NRL recommendation. A small sample subsequently prepared at NRL with these variations produced glass on which surface platinum contamination could not be detected microscopically. The variations are very likely not deleterious, but a final determination of this conclusion will have to be made by chemical analyses of improved samples to be submitted by the contractor. Work underway is concerned with the improvement of the optical quality of the glass.

IV. Publications

Luminescence Due to Impurity Traces in Silicate Glasses, R. J. Ginther and R. D. Kirk, J. of Non-Crystalline Solids 6, 89 (1971).

Laser Stimulated Thermoluminescence in Glass, R. J. Ginther and E. W. Claffy, J. of Applied Phys. 42, 4519 (1971).

Vacuum Ultraviolet Absorption in Alkali Doped Fused Silica and Silicate Glasses, G. H. Sigel, Jr., J. Phys. Chem. Solids 32, 2373 (1971).

The Role of Alkali in the Formation of Radiation-Induced Defect Centers in Simple Silicate Glasses, G. H. Sigel, Jr., Proceedings of Ninth International Congress on Glass, Vol. 1, 801 (1971).

Infrared Study of Boron Trichloride Chemisorbed on Silica Gel, V. M. Bermudez, J. Phys. Chem. 75, 3249 (1971).

Platinum Contamination of Glass, R. J. Ginther, accepted for publication in J. Non-Crystalline Solids.

Silica Glass: X-Ray Diffraction Evidence for a Tridymite-Like Structure, J. H. Konnert and J. Karle, submitted to Nature.

Bausch and Lomb

Optical Absorption and Color Caused by Selected Cations in High-Density Lead Silicate Glass, J. S. Stroud, J. Am. Ceram. Soc. 54, 401 (1971).

Optical Absorption of Lead in Glass, J. S. Stroud and E. Lell, J. Am. Ceramic Soc. 54, (1971).